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Wawzonek S, Blaha E W, Berkey R & Runner M E. Polarographic studies in acetonitrile and dimethylformamide. II. Behavior of aromatic olefins and hydrocarbons. *J. Electrochem. Soc.* 102:235-42, 1955.

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The electrochemical reduction of stilbene, anthracene, and *p*-anisylidene-fluorene in the aprotic solvents acetonitrile and dimethylformamide unexpectedly involved a stable anion-radical as an intermediate. Proof for this species was the formation of 1,2,3,4-tetraphenylbutane in the large-scale reduction of stilbene in dimethylformamide. The same reduction in the presence of carbon dioxide and of ethyl iodide gave *meso*-diphenylsuccinic acid and 1,2-diphenylbutane, respectively. [The SC7® indicates that this paper has been cited in over 150 publications since 1955.]

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"Polarographic and electrochemical studies of organic compounds prior to this work were limited to a great extent by their solubility and stability toward hydrolysis in mixtures of water and miscible organic solvents. The original intent of the cited work was to overcome these limitations by using anhydrous acetonitrile and dimethylformamide as solvents; both possibilities had dielectric constants of approximately 35 and were capable of dissolving tetrabutylammonium salts which were used as supporting electrolytes. These solvents overcame the limitations mentioned and in addition we found that stilbene, anthracene, and *p*-anisylidene-fluorene were reduced polarographically stepwise in two one-electron waves. Such a behavior was unexpected and implied that an anion-radical was formed as an intermediate which apparently combined with the solvent or reacted with the supporting electrolyte only very slowly. Such intermediates were prepared in the past by treating the aromatic hydrocarbon with an alkali metal in ether under nitrogen.

"The reactivity of the electrochemically generated anion-radical was demonstrated by studying the effect of water on the polarographic waves of stilbene. Addition of water caused the first wave to grow at the

expense of the second wave, and at a high enough concentration (2.44 percent) of water the two waves were replaced by one wave with a height equal approximately to the combined heights of the two waves obtained in anhydrous media.

"More conclusive evidence for the anion-radical was obtained from the nature of the products isolated from the large-scale electrochemical reduction of stilbene alone and in the presence of carbon dioxide and of ethyl iodide. The first of these when carried out in dimethylformamide gave a 30 percent yield of 1,2,3,4-tetraphenylbutane which would result from the hydrodimerization of the anion-radical. This dimerization was cited later as prior art by companies trying to invalidate the Monsanto patent for the electrochemical hydrodimerization of acrylonitrile to the important nylon intermediate adiponitrile.

"Electrochemical reduction of stilbene in the presence of carbon dioxide and of ethyl iodide gave *meso*-diphenylsuccinic acid and 1,2-diphenylbutane, respectively, which result from the reaction of the carbanion center of the anion-radical with the reagent used.

"The paper has been highly cited because (1) it fostered electrochemical studies of other types of compounds in aprotic solvents, and (2) it offered a new method for the preparation of anion-radicals for ESR studies and for acids. In the last category, studies of the electrochemical reduction of carbon dioxide found oxalic acid as the main product. The same reduction of carbon disulfide was more complex and gave, after methylation, 4,5-bis-(methylthio)-1,3-dithiole-2-thione. The mechanism of this compound involves the anion-radical of carbon disulfide.¹

"Based in part on this work I have received the Iowa Award and the Midwest Award of the American Chemical Society, the Outstanding Achievement Award of the University of Minnesota, and became a Distinguished Fellow of the Iowa Academy of Science.

"M.E. Runner was a postdoctorate fellow and E.W. Blaha and R. Berkey were graduate students who were supported by a grant from the Atomic Energy Commission. Runner is the only postdoctorate fellow who has worked for me in my long career."

1. Wawzonek S, Chang H, Everett W & Ryan M. Intermediates in the electrochemical reduction of carbon disulfide at a mercury cathode in aprotic solvents. *J. Electrochem. Soc.* 130:803-7, 1983.